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THE ARC SPECTRUM OF CHLORINE AND ITS STRUCTURE

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ABSTRACT

In the arc spectrum of Cl, emitted by an uncondensed discharge in a Geissler tube containing the gas at low pressure, more than 200 wave lengths were measured between the limits 4000 A in the violet and 9900 A in the infra-red. Sixty-two per cent of these lines, together with those observed by Turner in the Schumann region, have been classified as resulting from combinations between terms of the doublet and quartet systems. These terms arise mainly from the basic term ^3P of the ion, the terms coming from ^1S and ^1D not being definitely established, owing to the faintness of the lines. Nine sets of series-forming terms have been found. From these, the distance separating $^2P_2$, the base term of the neutral atom, from $^3P_2$, the lowest term of Cl^+, is found to be 104,991 cm$-^1$, giving 12.96 volts as the ionization potential of neutral chlorine.

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I. INTRODUCTION

In discussing the spectra of chlorine Kayser lists 114 papers dealing with this element in Volumes V and VII of the Handbuch. In Volume V, his summary of our knowledge of the chlorine spectra is: "Trotz mancher Untersuchungen ist das Spektrum des Chlors noch recht unbekannt." This estimate was changed but little on the appearance, in 1924, of Volume VII, which gives the wave-length measurements of Exner and Haschek.[1] Since this work was completed, however, several papers have appeared which have greatly extended our knowledge of the spectra, especially in the ultra-violet and beyond. These are by (1) Jevons,[2] who gives the wave lengths in I. A. of about 200 lines between the limits 3354 A and 2070 A; (2) Angerer,[3] whose work covers approximately the same region and is in good agreement with that of Jevons, although each author gives some lines not observed by the other; (3) Millikan and Bowen,[4] who for the first time present wave lengths in the extreme ultra-violet; (4) L. and E. Bloch,[5] who describe a method for separating the spectra according to the degree of ionization of the emitting particle; (5) Turner,[6] who presents seven lines characteristic of the arc spectrum lying in the Schumann region; (6) L. and E. Bloch,[7] whose earlier results are here extended to cover the region from 6850 A to 2202 A and consist mainly of lines belonging to Cl II and Cl III; (7) Vaudet,[8] whose wave lengths characterize various stages of spark spectra and extend the results of the Blochs from 2252 A to 1298 A; and (8) Bowen,[9] who gives new wave-length measurements of lines lying in the far ultra-violet and a classification of lines characteristic of Cl II, Cl III, Cl IV, and Cl V.

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[1] Die Spektren der Elemente bei normalem Druck, **III**, 1912. Franz Deuticke, Leipzig und Wien.

[2] Proc. Royal Soc. (London), A 103, p. 193; 1923.

[3] Zeit. für wiss. Phot., **22**, p. 200; 1924.

[4] Phys. Rev., **25**, p. 600; 1925.

In addition to these papers, describing hitherto unexplored regions of the spectrum, two other papers, one by Lunt,[10] the other by Asagoe,[11] describe the effect on the wave lengths of varying conditions of excitation. As a result of his studies Asagoe was able to distinguish three types of lines which he correctly interpreted as characteristic of the arc and spark spectra of chlorine.

II. EXPERIMENTAL PROCEDURE

At various times since September, 1922, the chlorine spectrum has been photographed at the Bureau of Standards for the purpose of extending our knowledge of the region of longer wave length. The work owed its inception to the appearance of many unknown lines on a spectrogram of an oxygen-filled Geissler tube obtained a year previously. The oxygen had been generated by heating a small amount of potassium perchlorate in a side tube attached to the discharge tube. These new lines, unidentifiable with any lines known at that time, were suspected as being due to chlorine, a suspicion subsequently proved correct.

In the present work the source employed for the chlorine exposures was a Geissler tube attached to a reservoir containing dry chlorine. Figure 1 is a schematic representation of the apparatus. The chlorine was generated by heating with a Bunsen flame dry auric chloride in the side tube *A*. The gas passed into the reservoir *B*, where it was dried over P_2O_5. From this bulb it could be admitted to the discharge tube *C* as needed. Owing to the rapid disappearance of the Cl within the discharge tube through combination with the metal of the electrodes, it was necessary at frequent intervals to replenish the gas within the tube from the reserve supply in the bulb *B*. When a tube had been in operation for several hours, a stage was reached approaching saturation, after which it would be necessary to admit gas from the reservoir only every three of four hours. But by this time the capillary was usually incrusted with a semitransparent film which greatly diminished the intensity of the light. Tubes were made either of pyrex or of fused quartz, the electrodes being disks of platinum 1 cm. in diameter and a millimeter in thickness.

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[5] Compt. Rend., **180**, p. 1740; 1925.
[6] Phys. Rev., **27**, p. 397; 1926.
[7] Ann. de Phys., **8**, p. 397; 1927.
[8] Compt. Rend., **185**, p. 1270; 1927.
[9] Phys. Rev., **31**, p. 34; 1928.
[10] Monthly Notices, Roy. Astron. Soc. **85**, p. 148; 1924.
[11] Mem. College Sci. Kyoto Imperial Univ., **10**, p. 15; 1926.

For the earlier series of observations the tubes were excited by a transformer which stepped up 100 volts a. c. to 10,000 volts. For the final series of observations a 40,000-volt transformer was used. Visual observations of the tubes, made with direct-vision spectroscopes, showed that the type of spectrum obtained depended both on the nature of the discharge and on the gas pressure within the tube. When an uncondensed discharge passed through the tube, with the gas pressure estimated under 20 mm Hg, the visual spectrum consisted of but few lines superposed on a background of faint continuous light, the color of the light in the capillary being pale red. If now the pressure of the gas was increased to 50 mm or more, many new lines, quite sharp and brilliant, appeared, the color of the capillary becoming grayish blue. Introduction of capacity of 0.006 μf caused the first type of lines to weaken and disappear in the faint continuous background; the lines of the second type became broadened and diffuse, while a third type of lines, sharp and brilliant,

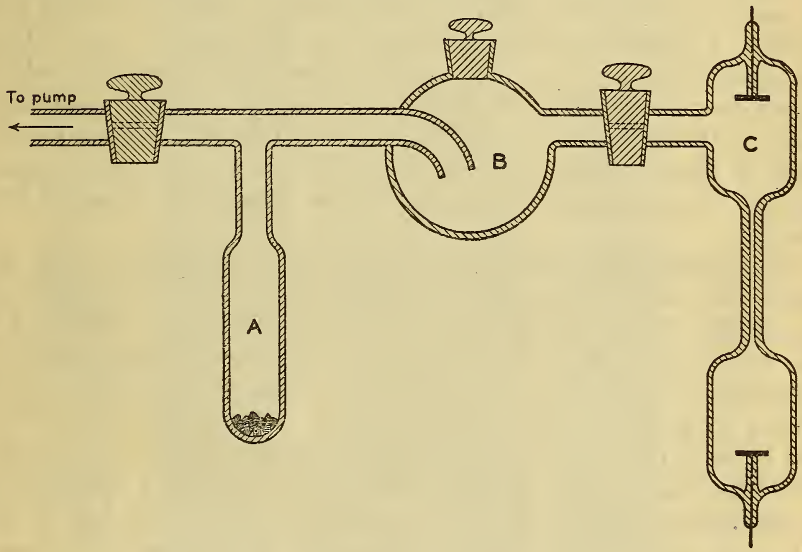

FIGURE 1.—*Chlorine generator and discharge tube used in studying the spectra of Cl.*

appeared. These observations are in accord with those reported by previous observers, notably Eder and Valenta,[12] Goldstein,[13] Nelthorpe,[14] and Asagoe.[15] We now know that these various types of lines are characteristic of the neutral and ionized stages of the chlorine atom.

Most of the spectrograms obtained in this investigation show at least two types of lines, since it was impossible to maintain, during the time necessary to make an exposure, the conditions favorable for the excitation of but one type. In Figure 2 is shown a portion of the spectrum extending from 4300 A to 4680 A. The upper spectrum was obtained with the uncondensed discharge in the gas at low pressure. This is the condition favorable for the excitation of the arc lines, a few of the more intense spark lines appearing, but indistinguishable in character from the arc lines. The lower spectrum illustrates the effect of a strongly condensed discharge on high-pressure gas. Here the spark lines are prominent and symmetrically broadened while the arc lines are diminished in intensity and asymmetrically broadened, sharp on the violet edge, and fading off toward the red. It was on the basis of these differences in the behavior of the lines that Asagoe effected his separation of the chlorine arc lines from those of the spark.

The spectrograms obtained in the present investigation were secured with the concave-grating spectrographs of the Bureau of Standards. These instruments have been frequently described.[16] The first order of the 20,000 lines per inch Rowland grating, giving a dispersion of 3.9 A per mm, was used to photograph the region from 2300 A to 5600 A. The Anderson grating, with a dispersion in the first order of 10.4 A per mm, was used in photographing the spectrum from 5200 A in the green to nearly 9900 A in the infra-red. Inasmuch as the filters used with the Anderson grating covered only half of the slit, each of the spectrograms thus obtained contained the overlapping second order in addition to the first-order spectrum. In all the observations the iron-arc spectrum was photographed to furnish the reference standards.

The earlier series of spectrograms were photographed on flat plates 20.5 cm long by 6.5 cm wide and coated with Seed 30 emulsion. For the later series of observations, both with the Rowland and with the Anderson gratings, either Schleussner ultra-rapid or Eastman 36 plates were used. These were 40 cm long by 6 cm wide and were on extra-thin glass so that they could be bent to fit the focal curves of the spectrographs. To render the plates sensitive to the green,

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[12] Beiträge zur Photochemie und Spektralanalyse, pp. 358–368; 1924, Wien.

[13] Astrophys. J., 27, p. 25; 1908.

[14] Astrophys. J., 41, p. 16; 1915.

[15] See footnote 11, p. 1118.

[16] B. S. Sci. Papers Nos. 312, 441, and 499.

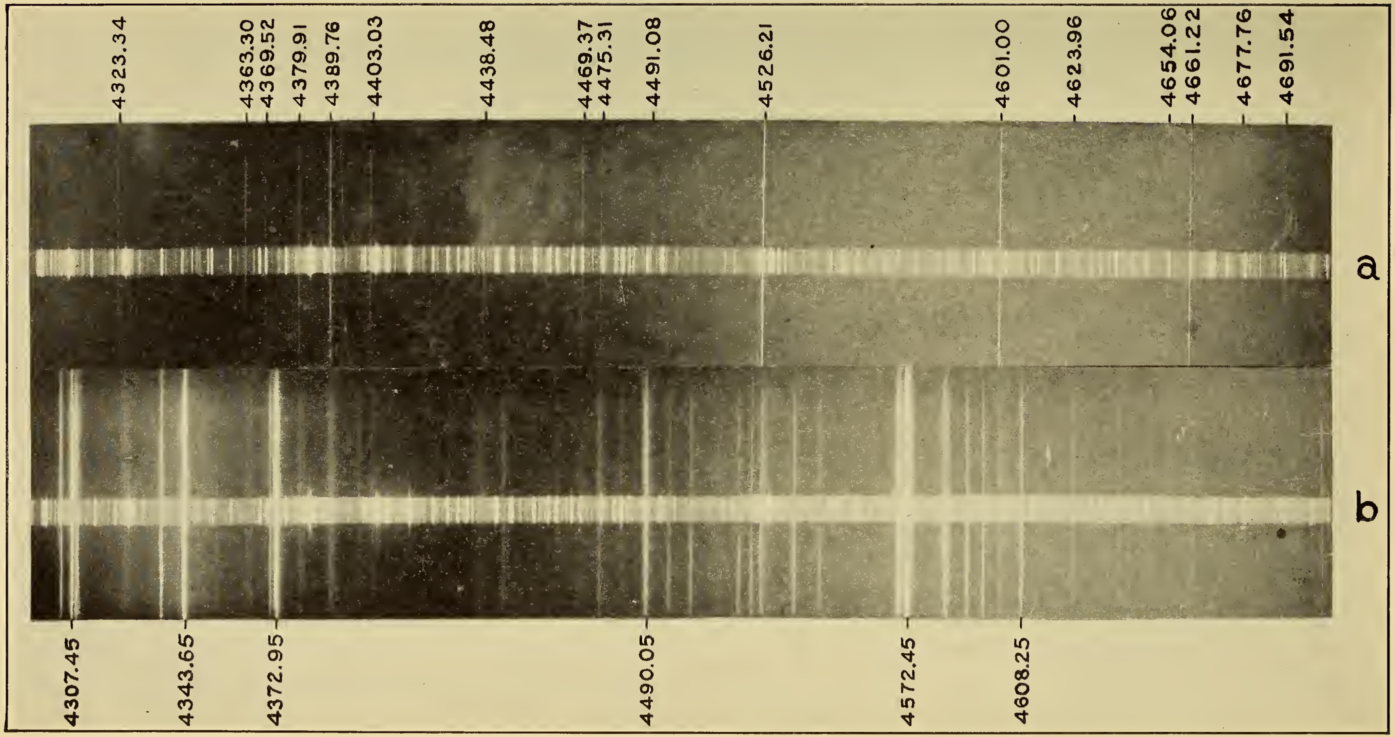

FIGURE 2.—*Arc and spark spectra of chlorine in the violet and blue*

a, Uncondensed discharge in gas at low pressure; *b,* condensed discharge in gas at high pressure

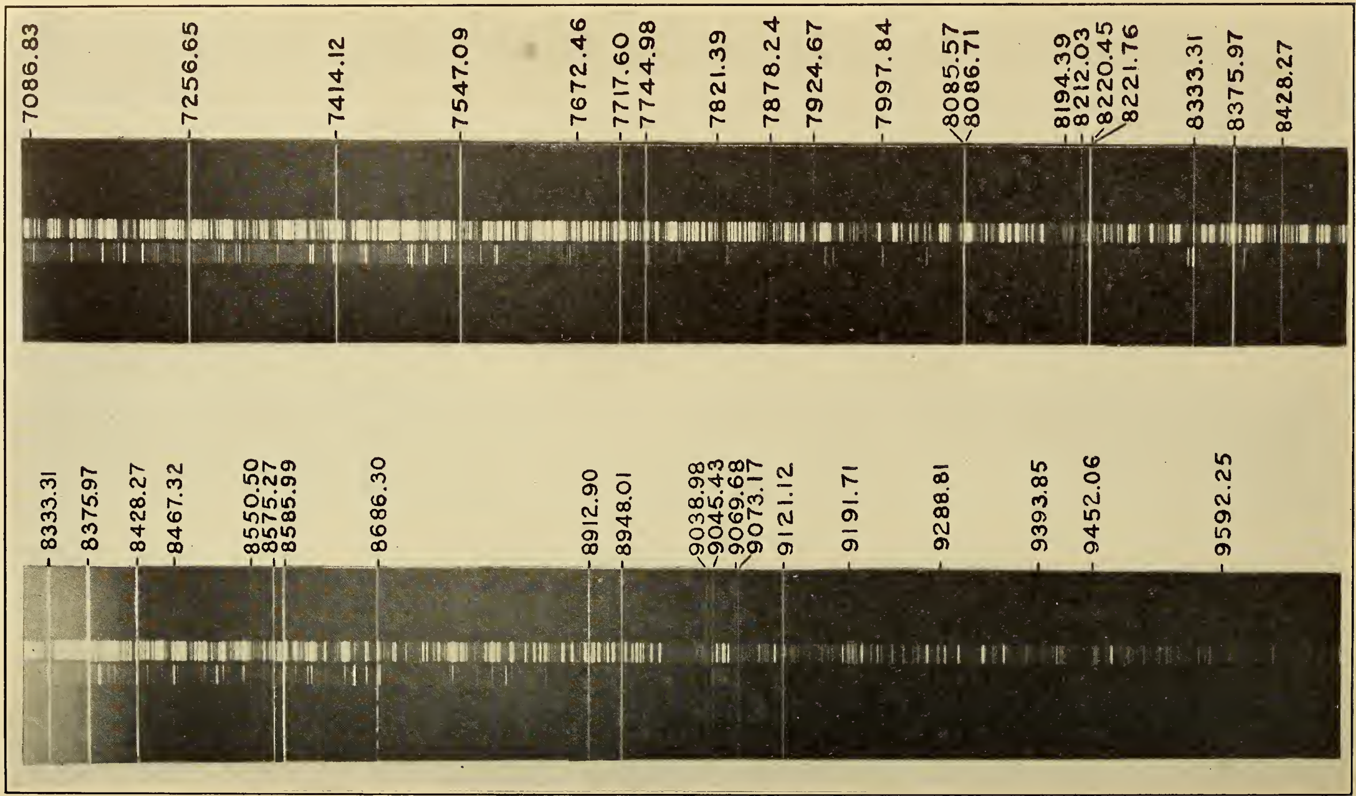

FIGURE 3.—*Arc spectrum of chlorine in the red and infra-red. First and second order Fe arc comparison spectrum*

yellow, red, and infra-red portions of the spectrum, they were bathed in solutions of pinaverdol, pinacyanol, dicyanin, and neocyanin, respectively, by the well-known methods.[17] The 40 cm plates when used with the Anderson grating cover a range of 4000 A in the first order. When these plates were used in photographing the region from 6400 A to 10000 A it was found that the following dye bath proved excellent in rendering them "panchromatic":

	ml
Water-alcohol mixture (85 parts H_2O+60 parts C_2H_5OH)	150. 0
Neocyanin solution (1:2000 in C_2H_5OH)	1. 5
Rubrocyanin solution (1:1000 in C_2H_5OH)	2. 0
Dicyanin solution (1:1000 in C_2H_5OH)	2. 5
Strong ammonia water	5. 0

The plate is soaked for five minutes in this bath and then rinsed for half a minute in alcohol, after which it is rapidly dried in a current of air. The plate from which Figure 3 was made was sensitized by this method. The uniformity of the sensitization can be judged from the exposure to the iron arc in the first order, which lasted five minutes and, on the original negative, can be followed to the line at 9307 A. The exposure times required to record the chlorine spectra ranged from a few minutes for the spark lines in the blue and violet to 15 hours for the infra-red arc lines.

III. RESULTS

The wave lengths derived from measurement of the spectrograms are given in the first column of Table 1. The majority of these wave lengths represent mean values obtained from 3 to 12 determinations, their relative accuracies being indicated by the letters in the third column, which have the following significance:

A = probable error of 0.000 A to 0.01 A.
B = probable error of 0.01 A to 0.02 A.
C = probable error of 0.02 A to 0.03 A.
D = probable error greater than 0.03 A.
E = only one determination.

Lines measured only once have been corrected by an amount necessary to reduce the other wave lengths of the same spectrogram to the mean of all the measurements. It is believed that all the lines listed in Table 1 are, with a few exceptions, characteristic of the neutral Cl atom. The doubtful lines appear to belong to iodine, and there is a possibility that some of the fainter lines may belong to the spectrum of Cl^+.

In addition to a few lines of silicon and the Balmer lines of hydrogen, the impurity lines which appeared on the spectrograms originated with the metals used for the lead-in wires of the Geissler tubes. In the quartz tubes these wires, to which the Pt electrodes were attached, were of molybdenum; and in the pyrex tubes, they were of tungsten. On the earlier spectrograms, lines of either Mo or W were prominent according to the tube used. In the later work, in which new tubes were employed, the precaution was taken of shielding the lead-in wires from the chlorine by covering them with a protective coating of glass. This procedure effectively eliminated the numerous lines of the two metals and gave spectra of chlorine in which the hydrogen lines appeared as the only impurity.

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[17] B. S. Sci. Paper No. 422.

TABLE 1.—*Wave lengths in the arc spectrum of chlorine*

λ I. A.	Intensity and notes	Wt.	ν	Term combinations
9876.08	1	E	10122.70	$4s^2P_1-4p^2D_2$
9702.30	1	E	10304.01	$4s^4P_1-4p^4P_2$
9592.25	2	C	10422.23	$4s^2P_2-4p^2D_3$
9584.80	0	E	10430.33	$4s^4P_2-4p^4P_3$
9486.88	0	E	10537.98	$4s^4P_1-4p^4P_1$
9452.06	3	B	10576.80	$4s^2P_1-4p^2P_2$
9393.85	1	E	10642.35	$4s^4P_2-4p^4P_2$
9288.84	4	A	10762.66	$4s^2P_2-4p^2D_2$
9197.47	1	D	10869.58	$4s^2P_1-4p^4S_2$
9191.71	5	B	10876.39	$4s^4P_2-4p^4P_1$
9121.12	8	A	10960.56	$4s^4P_3-4p^4P_3$
9073.17	6	B	11018.48	$4s^2P_1-4p^2S_1$
9069.68	4	B	11022.72	
9045.43	7	B	11052.28	$4s^2P_1-4p^2P_1$
9038.98	5	B	11060.16	
8948.01	10	A	11172.60	$4s^4P_3-4p^4P_2$
8912.90	8	A	11216.61	$4s^2P_2-4p^2P_2$
8846.07	0	E	11301.36	$4p^4D_2-3d^4D_3$
8711.45	0	E	11476.00	$4x22-5x26$
8686.30	8	A	11509.22	$4s^2P_2-4p^4S_2$
8641.80	0	E	11568.49	$4p^4D_3-3d^4D_4$
8628.58	0	E	11586.21	$4x21-5p^2D_2$
8589.08	0	E	11639.50	
8585.99	15	A	11643.69	$4s^4P_2-4p^4D_3$
8577.95	1	E	11654.60	$4p^4D_3-3d^4D_3$
8575.27	12	A	11658.24	$4s^4P_1-4p^4D_2$ $4s^2P_2-4p^2S_1$
8550.50	4	C	11692.02	$4s^2P_2-4p^2P_1$
8497.30	0	E	11765.21	$4p^4D_3-3d^4D_2$
8467.32	4	C	11806.87	$4p^4D_4-3d^4D_4$
8428.27	15	A	11861.57	$4s^4P_1-4p^4D_1$
8406.14	1	E	11892.83	$4p^4D_4-3d^4D_3$
8375.97	20	A	11935.64	$4s^4P_3-4p^4D_4$
8333.31	15	A	11996.74	$4s^4P_2-4p^4D_2$
8304.65	0	E	12038.14	$4p^2P_2-6s^4P_2$
8286.54	0	E	12064.45	
8280.82	0	E	12072.78	$4p^2D_3-5x25$
8273.64	0	E	12083.26	
8268.98	0	E	12090.07	
8267.39	0	E	12091.40	$4p^2P_2-3d^4F_3$
8258.30	0	E	12105.71	
8221.76	12	A	12159.51	$4s^4P_2-4p^2D_3$
8220.45	8	A	12161.44	$4s^4P_1-4p^2D_2$
8212.03	10	A	12173.91	$4s^4P_3-4p^4D_3$
8203.66	1	D	12186.34	
8200.23	5	B	12191.43	$4x22-5p^2P_1$
8199.06	5	B	12193.17	$4x21-5p^2P_1$
8194.39	7	A	12200.12	$4s^4P_2-4p^4D_1$
8170.02	0	E	12236.51	$4p^4D_2-5x25$
8148.74	0	E	12268.46	
8094.75	0	E	12350.30	

λ I. A.	Intensity and notes	Wt.	ν	Term combinations
8087.66	2	C	12361.12	$4x23-5p^2S_1$
8086.71	8	A	12362.57	
8085.57	6	A	12364.32	$4x22-5p^2S_1$
8084.51	4	A	12365.94	$4x21-5p^2S_1$
8051.03	2	B	12417.36	
8023.31	2	B	12460.26	
8017.54	1	E	12469.23	$4x23-5p^2P_2$
8015.58	4	B	12472.28	$4x22-5p^2P_2$
7997.84	6	A	12499.94	$4s^4P_2-4p^2D_2$
7980.61	1	E	12526.92	$4s^4P_3-4p^4D_2$
7976.97	3	B	12532.65	$4p^4P_1-3d^4D_2$
7974.74	2	C	12536.15	
7952.54	1	E	12571.15	
7935.01	2	C	12598.92	$4x21-5x25$
7933.88	4	B	12600.71	$4x22-5x25$
7924.67	8	A	12615.36	$4s^4P_1-4p^2P_2$
7915.10	3	B	12630.61	$4p^4P_1-3d^4D_1$
7899.36	5	B	12655.78	$4p^4P_2-3d^4D_3$
7878.24	8	A	12689.70	$4s^4P_3-4p^2D_3$
7840.66	0	E	12750.53	
7830.79	4	A	12766.60	$4p^4P_2-3d^4D_2$
7821.39	7	A	12781.94	$4p^4P_3-3d^4D_4$
7777.84	0	E	12853.51	
7771.13	1	E	12864.61	$4p^4P_2-3d^4D_1$
7769.18	4	A	12867.83	$4p^4P_3-3d^4D_3$
7744.98	10	A	12908.04	$4s^4P_1-4p^4S_2$
7717.60	9	A	12953.84	$4s^4P_2-4p^2P_2$
7702.87	1	E	12978.60	$4p^4P_3-3d^4D_2$
7692.94	0	E	12995.36	$4p^4D_2-6s^4P_2$
7672.46	5	B	13030.05	$4s^4P_3-4p^2D_2$
7659.47	0	E	13052.15	
7656.89	0	E	13056.54	$4s^4P_1-4p^2S_1$
7561.19	0	E	13221.80	
7547.09	12	A	13246.50	$4s^4P_2-4p^4S_2$
7492.10	3	B	13343.72	$4p^4D_4-6s^4P_3$
7489.46	2	B	13348.43	$4p^4D_3-6s^4P_2$
7462.40	2	B	13396.83	$4s^4P_2-4p^2S_1$ $4p^4D_4-3d^4F_5$
7459.46	1	E	13402.11	$4p^4D_3-3d^4F_3$
7454.23	0	E	13411.51	$4p^4D_1-6s^4P_1$
7444.35	1	E	13429.31	$4s^4P_2-4p^2P_1$
7435.68	2	B	13444.97	$4p^4D_4-3d^4F_4$
7414.12	12	A	13484.07	$4s^4P_3-4p^2P_2$
7382.50	1	E	13541.82	
7342.83	1	E	13615.00	$4p^4D_2-6s^4P_1$
7329.36	0	E	13640.00	$4p^4D_4-3d^4F_3$
7256.65	15	A	13776.67	$4s^4P_3-4p^4S_2$
7244.82	0	E	13799.16	
7195.04	1	E	13894.64	
7191.52	0	E	13901.44	
7094.29	1	D	14091.96	

TABLE 1.—*Wave lengths in the arc spectrum of chlorine*—Continued

λ I. A.	Intensity and notes	Wt.	ν	Term combinations
7086.83	3	B	14106.80	$4p^4P_2-6s^4P_3$
7008.18	1	E	14265.11	
6995.90	1	D	14290.15	
6981.90	2	A	14318.81	$4p^4P_3-6s^4P_3$
6966.95	1	D	14349.54	$4p^4P_2-6s^4P_2$
6932.94	3	A	14419.92	$4p^4P_3-3d^4F_4$
6854.50	0	D	14584.94	
6840.26	1	C	14615.30	$4p^4P_3-3d^4F_3$
6810.08	1	C	14680.07	
6709.96	1	C	14899.11	
6703.26	1	D	14914.01	
6678.45	1	C	14969.41	$4p^4P_2-6s^4P_1$
6653.85	0	C	15024.75	
6609.30	2	B	15126.03	
6604.61	2	B	15136.77	$4p^4D_3-4d^4D_3$
6600.14	0	E	15147.02	$4x22-4d^4D_3$
6542.42	2	B	15280.65	
6531.43	4	A	15306.36	$4p^4D_4-4d^4D_4$
6502.28	1	C	15374.98	$4p^4D_4-4d^4D_3$
6471.60	0	E	15447.87	
6453.34	0	E	15491.58	
6450.36	4	A	15498.74	$4p^2D_3-60$
6434.80	5	A	15536.21	
6425.64	2	B	15558.36	
6408.08	1	C	15600.99	
6398.64	7	A	15624.01	
6394.77	0	D	15633.47	
6371.48	0 Si?	D	15690.62	
6347.05	1	D	15751.00	
6341.70	3	B	15764.29	
6335.08	0	E	15780.77	
6321.65	1	B	15814.29	
6306.77	0	E	15851.60	
6291.86	0	E	15889.17	
6280.29	1	D	15918.44	
6252.34	2	C	15989.60	$4p^4P_1-4d^4D_2$
6242.66	1	C	16014.39	$4p^4D_3-60$
6231.57	2	B	16042.89	$4p^4P_1-4d^4D_1$
6226.48	0	D	16056.00	
6211.61	2	B	16094.44	$4p^4D_4-59$
6194.75	4	B	16138.24	$4p^4P_2-4d^4D_3$
6162.14	3	C	16223.65	$4p^4P_2-4d^4D_2$
6141.87	0	E	16277.19	$4p^4P_2-4d^4D_1$
6140.25	6	A	16281.49	$4p^4P_3-4d^4D_4$
6114.41	4	A	16350.29	$4p^4P_3-4d^4D_3$
6082.63	0 I?	C	16435.72	$4p^4P_3-4d^4D_2$
6028.38	0	E	16583.62	
6019.80	1	D	16607.26	
5991.46	0	E	16685.81	
5987.78	0	E	16696.07	
5965.74	0	E	16757.75	
5930.42	1	D	16857.55	$4p^4D_3-4d^4F_4$ $4p^4P_2-59$
5922.31	0	E	16880.64	
5913.82	0	E	16904.87	
5908.25	0	E	16920.81	$4p^4D_3-4d^4F_3$
5866.73	0	E	17040.56	
5856.74	2	B	17069.62	$4p^4P_3-59$
5847.74	2	C	17095.90	$4p^4D_4-4d^4F_4$
5846.71	2	C	17098.91	
5844.27	1	D	17106.04	
5842.40	0	E	17111.52	
5839.89	0	D	17118.88	
5806.86	0	E	17216.25	
5802.91	1	C	17227.97	$4p^4P_3-60$
5801.36	0	E	17232.57	
5799.94	3	B	17236.79	
5796.34	3	A	17247.49	
5774.84	0 I?	E	17311.71	
5772.65	0	E	17318.27	
5731.77	0	E	17441.79	
5726.27	0	E	17458.54	
5702.05	0	E	17532.70	
5686.38	0	E	17581.01	
5580.52	0	D	17914.51	
5578.22	1	C	17921.90	$4p^4P_2-4d^4F_3$
5569.17	2	D	17951.03	
5549.32	0	E	18015.24	
5532.16	3	C	18071.11	$4p^4P_3-4d^4F_4$
5528.09	0	D	18084.42	
5514.71	2	C	18128.30	
5513.00	2	C	18133.92	$4p^4P_3-4d^4F_3$
5493.28	1 I?	D	18199.02	
5405.74	0	E	18493.75	
5404.01	0	E	18499.65	
5341.04	1	E	18717.75	
5330.79	0	E	18753.74	
5307.62	0	E	18835.61	
5140.38	1	C	19448.41	$4s^2P_1-5x24$
4976.65	4	B	20088.25	$4s^2P_2-5x24$
4852.72	4	B	20601.26	$4s^2P_2-5p^4D_3$
4818.55	2	C	20747.35	$4s^2P_1-5p^4S_2$
4740.68	5	B	21088.14	$4s^2P_2-5p^4D_2$
4721.28	3	B	21174.79	$4s^2P_2-5p^2D_3$
4691.54	4	A	21309.02	$4s^2P_2-5p^4D_1$
4677.76	2	A	21371.79	$4s^2P_2-5x26$
4661.22	8	A	21447.62	$4s^2P_1-5p^2P_1$
4654.06	4	A	21480.62	$4s^2P_2-5p^2D_2$
4623.96	3	A	21620.45	$4s^2P_1-5p^2S_1$
4601.00	10	A	21728.34	$4s^2P_1-5p^2P_2$
4578.18	1	B	21836.64	$4s^4P_1-5p^4P_2$
4526.21	12	A	22087.37	$4s^2P_2-5p^2P_1$
4491.08	4	A	22260.14	$4s^2P_2-5p^2S_1$
4475.31	6	A	22338.57	$4s^4P_2-5p^4D_3$
4469.37	6	A	22368.26	$4s^2P_2-5p^2P_2$
4446.12	2	B	22485.23	$4s^4P_2-5p^4P_1$
4445.82	2	B	22486.75	$4s^4P_1-5p^4D_2$
4438.48	7	A	22523.93	$4s^4P_3-5p^4P_3$
4403.03	6	A	22705.28	$4s^4P_3-5p^4P_2$
4402.52	1	E	22707.91	$4s^4P_1-5p^4D_1$
4390.38	4	A	22770.70	$4s^4P_1-5x26$
4389.76	12	A	22773.91	$4s^4P_3-5p^4D_4$
4387.53	3	A	22785.49	$4s^4P_1-5p^4S_2$
4379.91	7	A	22825.13	$4s^4P_2-5p^4D_2$
4371.55	1	B	22868.78	$4s^4P_3-5p^4D_3$
4369.52	6	A	22879.40	$4s^4P_1-5p^2D_2$
4363.30	6	A	22912.02	$4s^4P_2-5p^2D_3$
4323.34	6	A	23123.79	$4s^4P_2-5p^4S_2$
4264.58	3	A	23442.39	$4s^4P_3-5p^2D_3$
4226.43	5	A	23653.99	$4s^4P_3-5p^4S_2$
4209.67	4	A	23748.17	$4s^4P_3-5p^2D_2$
4208.00	2	B	23757.59	
4185.52	1	B	23885.19	
4032.19	2	A	24793.44	

IV. STRUCTURE OF THE ARC SPECTRUM

According to the spectroscopic alternation law, the arc spectrum of chlorine should consist of multiplets representing combinations of terms of even multiplicity. These terms, in accordance with Hund's theory, arise from the various configurations assumed by the seven valence electrons which lie outside the closed shells of the preceding rare gas, neon. In the unexcited state of the Cl atom two of these electrons occupy 3_1 orbits, and five are assigned to 3_2 orbits, which is expressed by the symbol s^2p^5. The term which is therefore characteristic of the normal state is an inverted ^{2}P; that is, the component with inner quantum number $j=3/2$ lies lowest. Throughout this paper the use of cumbersome fractional inner quantum numbers is avoided by assigning to each term an integral inner quantum number one-half unit greater than the true value.

The terms which represent the excited states of the atom result from the interaction of the series electron with the electron group s^2p^4 which characterizes the unexcited state of the ion Cl$^+$. The terms arising from the configuration s^2p^4 are ^{1}S, ^{1}D, and ^{3}P, of which the latter is lowest and has already been established for Cl II by Bowen.[18] We may therefore obtain the terms representing the excited states of the neutral atom by finding the resultants gotten by adding in turn the electrons *ns*, *np*, *nd*, etc., to the terms ^{1}S, ^{1}D, and ^{3}P. In Table 2 are given the theoretical terms which may be expected to account for the lines presented in Table 1.

TABLE 2.—*Theoretical terms of Cl I*

Electron configuration	Basic term of Cl II		
	^{3}P	^{1}D	^{1}S
$3s^2 . 3p^5$	$^2\mathbf{P}$		
$3s^2 . 3p^4 . 3d$	^{2}P, ^{2}D, ^{2}F, ^{4}P, $^4\mathbf{D}$, $^4\mathbf{F}$	^{2}S, ^{2}P, ^{2}D, ^{2}F, ^{2}G	^{2}D
$3s^2 . 3p^4 . 4s$	$^2\mathbf{P}$, $^4\mathbf{P}$	^{2}D	^{2}S
$3s^2 . 3p^4 . 4p$	$^2\mathbf{S}$, $^2\mathbf{P}$, $^2\mathbf{D}$, $^4\mathbf{S}$, $^4\mathbf{P}$, $^4\mathbf{D}$	^{2}P, ^{2}D, ^{2}F	^{2}P
$3s^2 . 3p^4 . 4d$	^{2}P, ^{2}D, ^{2}F, ^{4}P, $^4\mathbf{D}$, $^4\mathbf{F}$	^{2}S, ^{2}P, ^{2}D, ^{2}F, ^{2}G	^{2}D
$3s^2 . 3p^4 . 5s$	^{2}P, ^{4}P	^{2}D	^{2}S
$3s^2 . 3p^4 . 5p$	$^2\mathbf{S}$, $^2\mathbf{P}$, $^2\mathbf{D}$, $^4\mathbf{P}$, $^4\mathbf{P}$, $^4\mathbf{D}$	^{2}P, ^{2}D, ^{2}F	^{2}P
$3s^2 . 3p^4 . 6s$	^{2}P, $^4\mathbf{P}$	^{2}D	^{2}S

The terms which have actually been found for Cl I are given in Table 3. It has been possible to identify most of these terms with the theoretical ones of Table 2, and wherever this has been done the fact is indicated in Table 2 by printing the symbol in heavy type. Complex terms of Cl I which are based on ^{3}P of the ion may be expected to have widely separated components, whereas terms derived from ^{1}S and ^{1}D will exhibit only narrow separations. An inspection of Table 3 shows that most of the terms listed therein are based on

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[18] Phys. Rev., **31**, p. 34; 1928.

^{3}P, the others apparently originating either with ^{1}S or ^{1}D. The uncertainty of establishing the origin of these terms, giving groups of lines with fine structure, is discussed below. No comment is needed to interpret Table 3 other than to state that the numerical values of the terms are absolute; that is, they are based on what is believed to be the most probable value of the ground term $^2P_2$. The derivation of this value from the series limits is described in a subsequent paragraph. Figure 4 illustrates graphically the data of Table 3.

TABLE 3.—*Terms of Cl I*

Term No.	Term type	ν	$\Delta\nu$	Series electron	Term No.	Term type	ν	$\Delta\nu$	Series electron
1	$^2P_2$	104991.	881.	3*p*	31	$^4D_3$	10168. 25	486. 68	5*p*
2	$^2P_1$	104110.			32	$^4D_2$	9681. 57	221. 08	
3	$^4P_3$	33037. 00	530. 20	4*s*	33	$^4D_1$	9460. 49		
4	$^4P_2$	32506. 80	338. 44		34	$^4S_2$	9382. 70		
5	$^4P_1$	32168. 36			35	$^2D_3$	9594. 69	305. 70	
6	$^2P_2$	30769. 56	639. 80		36	$^2D_2$	9288. 99		
7	$^2P_1$	30129. 76			37	$^2P_2$	8682. 16	280. 80	
8	$^4P_3$	22076. 46	212. 05	4*p*	38	$^2P_1$	8401. 36		
9	$^4P_2$	21864. 41	233. 96		39	$^2S_1$	8509. 37		
10	$^4P_1$	21630. 45			40	$^4D_4$	9294. 51	85. 92	3*d*
11	$^4D_4$	21101. 36	238. 26		41	$^4D_3$	9208. 59	110. 75	
12	$^4D_3$	20863. 10	353. 01		42	$^4D_2$	9097. 84	98. 02	
13	$^4D_2$	20510. 09	203. 36		43	$^4D_1$	8999. 82		
14	$^4D_1$	20306. 73			44	$^4F_5$	?		
15	$^2D_3$	20347. 31	340. 35		45	$^4F_4$	7656. 40	195. 25	
16	$^2D_2$	20006. 96			46	$^4F_3$	7461. 15		
17	$^2P_2$	19552. 96	475. 40		47	$^4F_2$	?		
18	$^2P_1$	19077. 56			48	$^4P_3$	7757. 63	242. 83	6*s*
19	$^4S_2$	19260. 32			49	$^4P_2$	7514. 80	619. 76	
20	$^2S_1$	19111. 28			50	$^4P_1$	6895. 04		
21	^2X	20875. 32	1. 70	4*x*	51	$^4D_4$	5794. 98	68. 69	4*d*
22	^2X	20873. 62	3. 08		52	$^4D_3$	5726. 29	85. 51	
23	^2X	20870. 54			53	$^4D_2$	5640. 78	53. 39	
24		10681. 33		5*x*	54	$^4D_1$	5587. 39		
25		8274. 65			55	$^4F_5$	?		
26		9397. 72			56	$^4F_4$	4005. 40	62. 87	
27	$^4P_3$	10513. 07	181. 35	5*p*	57	$^4F_3$	3942. 53		
28	$^4P_2$	10331. 72	310. 15		58	$^4F_2$	?		
29	$^4P_1$	10021. 57			59	?	5006. 88		
30	$^4D_4$	10263. 09	94. 84		60	?	4848. 59		

Since no Zeeman effects are available to reveal the identity of the chlorine arc lines, the classification of the lines into multiplets had to be based mainly on the evidence furnished by recurring constant wave-number differences, line intensities, and analogies with other spectra whose structures are theoretically the same as that of Cl I. The important $\Delta\nu$'s to be sought for were revealed to some extent by Turner's lines and by the earlier investigations of de Bruin,[19] who found the separation $\Delta\nu = 530.2$ occurring conspicuously among the lines ascribed to the arc by Nelthorpe. The constant differences discovered by Paulson,[20] which are real, appear to be characteristic of spark lines only.

In Tables 4 to 9 are presented the principal multiplets which contain most of the prominent lines of Cl I. In many of the multiplets the full complement of lines has not been observed. These fainter lines, whose wave lengths may be calculated from the term combinations, are indicated in the tables by braces $\left\{\quad\right\}$. The resonance lines lie in the Schumann region and were first observed by Turner. The interpretation of these lines as resulting from the electron transition $4s \rightarrow 3p$ has already been announced by Bowen [21] and by Laporte.[22] The prominent multiplets lying in the near infra-red, shown in Table 5, represent the transition of the series electron from the $4p$ state to the $4s$ state. It is to be noted that among these the intersystem combination $^2P_2 - {}^4P_{1\,2\,3}$ is very strong. It is to be noted further that the separations of the $4p$ terms (^4D, ^4P) deviate strongly from the Landé interval rule. This indicates an anomalous coupling which becomes much more developed with the $5p$ terms and makes it difficult to identify those of the quartet system. The combinations which have been found lie in the blue and violet and are set forth in Table 6.

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[19] K. Akad. Wet. Amsterdam, **30**, p. 20; 1926. Zeit. für Physik, **39**, p. 869; 1926.

[20] Astrophys. J., **40**, p. 298; 1914.

[21] Phys. Rev., **31**, p. 498; 1928.

[22] Nature, **121**, p. 1021; 1928.

It seems probable that the infra-red lines with fine structure, Table 7, represent combinations between the 5*p* doublet terms and terms arising from ^{1}D or ^{1}S of the ion. A satisfactory identification of these terms, numbered 21, 22, and 23, in Table 10, has not yet been found. They are shown in Figure 4 on the line labeled ^{2}X and should consist of at least two term groups if the parent term of the ion is ^{1}S or ^{1}D.

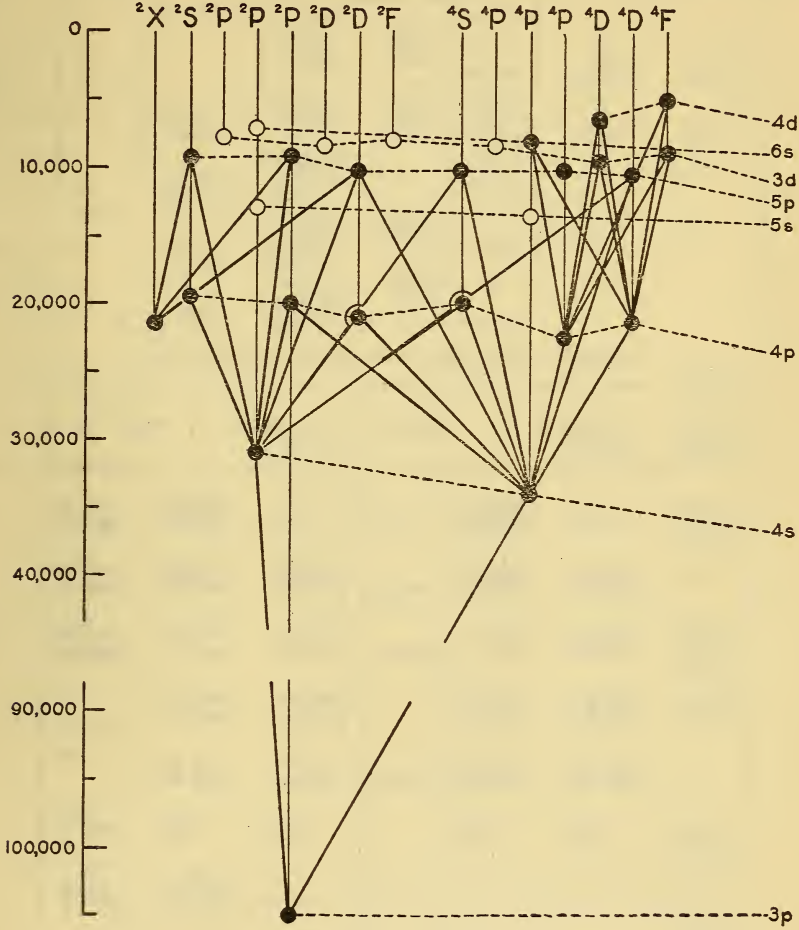
^{2}X ^{2}S ^{2}P ^{2}P ^{2}P ^{2}D ^{2}D ^{2}F
^{4}S ^{4}P ^{4}P ^{4}P ^{4}D ^{4}D ^{4}F
0
10,000
20,000
30,000
40,000
90,000
100,000
4d
6s
3d
5p
5s
4p
4s
3p

FIGURE 4.—*Term diagram of Cl I*

TABLE 4.—*Turner's lines*

$3p$ / $4s$	$^2P_1$	881	$^2P_2$
$^2P_2$	5 1363.5 73342		5 1347.2 74225
639.80			
$^2P_1$	3 1351.7 73979		2 1335.8 74863
$^4P_3$			{1389.8 71954}
530.20			
$^4P_2$	3 1396.5 71607		5 1379.6 72484
338.44			
$^4P_1$	4 1389.9 71946		{1373.2 72825}

TABLE 5.—*Multiplets from the transition $4p \rightarrow 4s$*

$4s$ / $4p$	$^2P_1$	639.80	$^2P_2$	1398.80	$^4P_1$	338.40	$^4P_2$	530.20	$^4P_3$
$^2D_3$			2 9592.25 10422.23				12 8221.76 12159.51		8 7878.24 12689.70
340.35									
$^2D_2$	1 9876.08 10122.70		4 9288.84 10762.66	1398.78	8 8220.45 12161.44		6 7997.84 12499.94		5 7672.46 13030.05
$^2P_2$	3 9452.06 10576.80		8 8912.90 11216.61	1398.75	8 7924.67 12615.36		9 7717.60 12953.84		12 7414.12 13484.07
475.40									
$^2P_1$	7 9045.43 11052.28		4 8550.50 11692.02		{7636.8 13090.8}		1 7444.35 13429.31		
$^2S_1$	6 9073.17 11018.48		12 8575.27 11658.24	1398.30	0 7656.89 13056.54		2 7462.40 13396.83		
$^4D_4$									20 8375.97 11935.64
238.26									
$^4D_3$							15 8585.99 11643.69		10 8212.03 12173.91
353.01									
$^4D_2$					12 8575.27 11658.24		15 8333.31 11996.74		1 7980.61 12526.92
203.36									
$^4D_1$					15 8428.27 11861.57		7 8194.39 12200.12		
$^4P_3$							0 9584.80 10430.33		8 9121.12 10960.56
212.05									
$^4P_2$					1 9702.30 10304.01		1 9393.85 10642.35		10 8948.01 11172.60
233.96									
$^4P_1$					0 9486.88 10537.98		5 9191.71 10876.39		
$^4S_2$	1 9197.47 10869.58		8 8686.30 11509.22	1398.82	10 7744.98 12908.04		12 7547.09 13246.50		15 7256.65 13776.67

TABLE 6.—*Multiplets from the transition 5p→4s*

5p \ 4s	$^2P_1$	639.80	$^2P_2$	1398.80	$^4P_1$	338.40	$^4P_2$	530.20	$^4P_3$
$^2D_3$			3 4721.28 21174.79				6 4363.30 22912.02		3 4264.58 23442.39
305.70									
$^2D_2$	{4796.9 20840.8}		4 4654.06 21480.62	1398.78	6 4369.52 22879.40		1 4305.87 23217.60		4 4209.67 23748.17
$^2P_2$	8 4661.22 21447.62		12 4526.21 22087.37						
280.80									
$^2P_1$	10 4601.00 21728.34		6 4469.37 22368.26						
$^2S_1$	3 4623.96 21620.45		4 4491.08 22260.14						
$^4D_4$									12 4389.76 22773.91
94.84									
$^4D_3$			4 4852.72 20601.26				6 4475.31 22338.57		1 4371.55 22868.78
486.68									
$^4D_2$	{4889.1 20448.1}		5 4740.68 21088.14	1398.61	2 4445.82 22486.75		7 4379.91 22825.13		{4280.5 23355.3}
221.08									
$^4D_1$	{4836.7 20669.2}		4 4691.54 21309.02	1398.89	1 4402.52 22707.91		{4337.9 23046.3}		
$^4P_3$							{4545.5 21993.7}		7 4438.48 22523.93
181.35									
$^4P_2$					1 4578.18 21836.64		{4508.3 22175.0}		6 4403.03 22705.28
310.15									
$^4P_1$					{4514.1 22146.8}		2 4446.12 22485.23		
$^4S_2$	2 4818.55 20747.35		{4674.4 21386.8}		3 4387.53 22785.49		6 4323.34 23123.79		5 4226.43 23653.99

TABLE 7.—*Combinations of doublet terms with fine-structure terms*

4x \ 5p	$^2S_1$	$^2P_1$	$^2P_2$	$^2D_2$	$^2D_3$
21	4 8084.51 12365.94	5 8199.06 12193.17		0 8628.58 11586.21	
1.70					
22	6 8085.57 12364.32	5 8200.23 12191.43	4 8015.58 12472.28		
3.08					
23	2 8087.66 12361.12		1 8017.54 12469.23		

TABLE 8.—*Multiplets from the transition $3d \rightarrow 4p$*

$4p$ $3d$	$^4P_1$	233.96	$^4P_2$	212.05	$^4P_3$	$^4D_1$	203.36	$^4D_2$	353.01	$^4D_3$	238.26	$^4D_4$
$^4D_4$					7 7821.39 12781.94					0 8641.80 11568.49		4 8467.32 11806.87
85.92												
$^4D_3$			5 7899.36 12655.78		4 7769.18 12867.83			0 8846.07 11301.36		1 8577.95 11654.60		1 8406.14 11892.83
110.75												
$^4D_2$	3 7976.97 12532.65		4 7830.79 12766.60		1 7702.87 12978.60	{8919.2 11208.7}		{8760.2 11412.1}		0 8497.30 11765.21		
98.02												
$^4D_1$	3 7915.10 12630.61		1 7771.13 12864.61			{8841.9 11306.7}		{8685.6 11510.1}				
$^4F_5$												2 7462.40 13396.83
?												
$^4F_4$					3 6932.94 14419.92					{7569.8 13206.7}		2 7435.68 13444.97
195.25												
$^4F_3$			{6940.9 14403.3}		1 6840.26 14615.30			{7661.3 13049.1}		1 7459.46 13402.11		0 7329.36 13640.00
?												
$^4F_2$	{6818.4 14662.1}		{6711.4 14896.0}		{6617.1 15108.1}	{7495.1 13338.4}		1 7382.50 13541.82		1 7195.04 13894.64		

TABLE 9.—*Multiplets from the transitions $4d \rightarrow 4p$ and $6s \rightarrow 4p$*

$4p$ $4d$	$^4P_1$	233.96	$^4P_2$	212.05	$^4P_3$	$^4D_1$	203.36	$^4D_2$	353.01	$^4D_3$	238.26	$^4D_4$
$^4D_4$					6 6140.25 16281.49					{6634.7 15068.1}		4 6531.43 15306.36
68.69												
$^4D_3$			4 6194.75 16138.24		4 6114.41 16350.29			{6762.3 14783.8}		2 6604.61 15136.77		1 6502.28 15374.98
85.51												
$^4D_2$	2 6252.34 15989.60		3 6162.14 16223.65		0 6082.63 16435.72	{6816.7 14665.8}		{6723.5 14869.2}		{6567.6 15222.2}		
53.39												
$^4D_1$	2 6231.57 16042.89		0 6141.87 16277.19			{6792.0 14719.2}		{6699.4 14922.6}				
$^4F_5$												?
?												
$^4F_4$					3 5532.16 18071.11					1 5930.42 16857.55		2 5847.74 17095.90
62.93												
$^4F_3$			1 5578.22 17921.90		2 5513.00 18133.92			{6034.1 16567.8}		0 5908.25 16920.81		{5826.2 17159.1}
?												
$^4F_2$	?		?		?	?		?		?		
$4p$ $6s$												
$^4P_3$			3 7086.83 14106.80		2 6981.90 14318.81			{7839.5 12752.4}		{7628.3 13105.4}		3 7492.10 13343.72
242.83												
$^4P_2$	{7082.0 14115.5}		1 6966.95 14349.54		0 6865.50 14561.57	{7815.2 12792.0}		0 7692.94 12995.36		2 7489.46 13348.43		
619.76												
$^4P_1$	{6784.5 14735.4}		1 6678.45 14969.41			0 7454.23 13411.51		1 7342.83 13615.00				

TABLE 10.—*Series limits of Cl I*

Term sequence	Limiting term of Cl^+			$^2P_2-^3P_2$
	$^3P_0$	$^3P_1$	$^3P_2$	
$4p, 5p, ^2P_2$	106491			105493
$4p, 5p, ^2P_1$		106661		105963
$4s, 6s, ^4P_3$			104723	104723
$4s, 6s, ^4P_2$			104920	104920
$4s, 6s, ^4P_1$		105573		104875
$4p, 5p, ^4P_3$			105001	105001
$4p, 5p, ^4P_2$			105167	105167
$4p, 5p, ^4P_1$		105516		104818
$4p, 5p, ^4D_4$			104890	104890
$4p, 5p, ^4D_3$			104911	104911
$4p, 5p, ^4D_2$			105467	105467
$4p, 5p, ^4D_1$			105697	105697
$4p, 5p, ^2D_3$		105524		104826
$4p, 5p, ^2D_2$		105602		104904
$4p, 5p, ^4S_2$		105269		104571
$4p, 5p, ^2S_1$	106082			105084
$3d, 4d, ^4D_4$			104578	104578
$3d, 4d, ^4D_3$			104635	104635
$3d, 4d, ^4D_2$			104695	104695
$3d, 4d, ^4D_1$			104709	104709
$3d, 4d, ^4F_4$			104964	104964
$3d, 4d, ^4F_3$			104914	104914
Means	106286	105691	104948	104991
$^3P_0-^3P_1 : ^3P_1-^3P_2$ $\begin{cases}\text{calculated } 595:743\\ \text{observed } 300:698\end{cases}$				
Ionization potential $=1.2345\times104991\times10^{-4}=12.96v$				

The ^4P and ^4D terms coming from the $4p$ electron combine with higher ^4P, ^4D, and ^4F terms, coming from the $3d$, $6s$, and $4d$ electrons, to give the multiplets of Tables 8 and 9. The identity of the $4d$ electron is not absolutely certain. The ^4D and ^4F terms could, as well, come from a $4f$ electron. But we are inclined to the belief that it is $4d$ for the following reasons: (1) There is a close parallelism between the intensities of the lines in the multiplets arising from it and the corresponding ones coming from the $3d$ electron; (2) the term separations are all smaller than in $3d$ ^4D, which is a necessary characteristic (discussed below) of nd ^4D terms in Rydberg sequence and approaching a common limit in the ion; (3) the values for the series limits from these terms, on the assumption that they are in sequence, are in excellent accord with those given by the other series.

The terms coming from the $5s$ electron have not been found. Of these, the more prominent would be ^2P and ^4P, with values lying between 13,000 and 15,000. Their combinations, therefore, with the terms arising from the $4p$ and $5p$ electrons would fall in the infra-red beyond the domain accessible to the sensitized photographic plate.

In Figure 4 series-forming terms are plotted on the same vertical line. An inspection of the figure shows at least seven sets of terms which are available for calculating series limits, and nine if the terms ^4D and ^4F are correctly attributed to the $4d$ electron. In only one sequence are more than two terms known. For this reason it did not seem justifiable to seek more accurate values for the terms than those to be found by substitution in Rydberg's formula.

The solution is readily effected by the use of a suitable table such as Table 3 of Fowler's Report. By adding to the term values thus obtained the amounts of their relative separations from the basic term $^2P_2$ we obtain the distances between the limiting terms of the ion and the lowest term of the neutral atom. The limits to which the component series converge are the components of the ground term $^3P_{0,1,2}$ of the ion. This term, established for Cl II by Bowen, is characterized by the separations $\Delta\nu_{0,1}=300$, $\Delta\nu_{1,2}=698$, the component $^3P_2$ being lowest. In Table 10 the values found from all the component series are presented. It is seen that only two values are available for fixing the position of $^3P_0$. Of these, the first appears to be erratic and when averaged with the other gives a value for the difference $^3P_0-{}^3P_1$ nearly twice that found by observation. The value of the difference $^3P_1-{}^3P_2$, however, from the calculated series limits is in excellent agreement with that observed. The observed separations $^3P_1-{}^3P_2=698$ and $^3P_0-{}^3P_2=998$ have been applied to the individual determinations of the limits $^3P_1$ and $^3P_0$ to give the value of the limit $^3P_2$. The mean value found for the separation of the lowest levels of the neutral atom and the ion is $^2P_2-{}^3P_2=104991$ cm^{-1}, and from this an ionization potential of 12.96 volts is derived. This value differs only slightly from the value 13.0 volts found by linear interpolation between the ionization potentials of 10.31 volts for S I. (Hopfield) [23] and 15.69 volts for A I. (Meissner).[24]

Based on theoretical considerations, Hund [25] has given a schematic representation of the structure of a halogen spectrum and has indicated the manner in which the various series approach their limits. That his procedure did not lead to correct results for spectra built up on inverted terms has already been pointed out by Shenstone [26] for Ne, Ni, Pd, and other spectra. With the detection of the higher series terms of Cl I we saw that for this spectrum also Hund's procedure would not give correct results. For instance, the term separations (530.20; 338.40) of $4s\ ^4P_{3,2,1}$ and (242.83; 629.76) of $6s\ ^4P_{3,2,1}$ indicate that in approaching the limit the separation $\Delta\nu_{3,2}$ decreases while $\Delta\nu_{2,1}$ increases. If Hund's scheme were correct, we should expect $\Delta\nu_{3,2}$ to increase and $\Delta\nu_{2,1}$ to decrease. It may be noted here, in this connection, that we have found in Br I this anomalous coupling appears in the term $5s\ ^4P_{3,2,1}$, which is analogous to $4s\ ^4P_{3,2,1}$ of Cl I, the separation $\Delta\nu_{3,2}$ being smaller than $\Delta\nu_{2,1}$. It is thus clear that in the series of ^4P terms coming from the *ns* electrons the components $^4P_{3,2}$ approach $^3P_2$ of the ion as limit, and $^4P_1$ approaches $^3P_1$ as limit.

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[23] Nature, **112**, p. 437; 1923.

[24] Zeit. für Physik, **40**, p. 844; 1927.

[25] Linienspektren und periodisches System der Elemente, p. 198; 1927. Julius Springer, Berlin.

[26] Phys. Rev., **39**, p. 380; 1927. Nature, **121**, p. 619; 1928; **122**, p. 727; 1928.

Again, in the series of ^4P terms coming from the *np* electrons we observe that the separations $\Delta\nu_{3,2}$ are smaller than $\Delta\nu_{2,1}$, which we interpret as indicating that the components $^4P_{3,2}$ approach $^3P_2$ of Cl II as limit, and $^4P_1$ approaches $^3P_1$ as limit.

We find that the identification of series limits just presented is in strict harmony with the new theoretical considerations of Hund[27] which have just come to our notice. For series terms coming from the *s* and *p* electrons his revised scheme is as follows:

$p^2P_2,\ p^2S_1,\ s^2P_1$ -- $\rightarrow$ $^3P_0$
$p^4P_1,\ p^4S_2,\ p^2D_{3,2},\ p^2P_1,\ s^4P_1,\ s^2P_2$ -------------------- $\rightarrow$ $^3P_1$
$p^4D_{4,3,2,1},\ p^4P_{3,2},\ s^4P_{3,2}$ ------------------------------ $\rightarrow$ $^3P_2$

To show the manner in which series terms coming from *nd* electrons approach their limits, we have extended Hund's scheme as follows:

$^2P_{2,1}$ -- $\rightarrow$ $^3P_0$
$^4P_{2,1},\ ^2D_{3,2},\ ^2F_{4,3}$ -------------------------------- $\rightarrow$ $^3P_1$
$^4P_3,\ ^4D_{4,3,2,1},\ ^4F_{5,4,3,2}$ ---------------------------- $\rightarrow$ $^3P_2$

It is thus seen that all the components of ^4D series approach a common limit, which means that the term separations of the higher series members become progressively smaller. It is this fact that has induced us to regard the ^4D and ^4F terms, discussed above, as belonging to the *nd* sequence.

No Zeeman effects for chlorine arc lines have ever been observed. The few observations published by Kimura and Fukuda[28], refer only to spark lines. In view of this situation we have relied on the analogies afforded by the first spark spectrum of argon, of which the structure has been worked out by deBruin[29], and confirmed by Zeeman effects, to work out the classification of Cl I described above. And the conclusions thus arrived at have been further strengthened on the detection by deBruin[30], of similar structures in the spectrum K III.

Theoretically the structures of Cl I and A II should be similar. The extent to which the actual classification of the spectra bears out the similarity may be seen by comparing the term diagram of Cl I (fig. 4) with that of A II given by deBruin in the work referred to. The following table gives a comparison of the corresponding term separations.

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[27] Zeit. für Physik, **52**, p. 601; 1928.

[28] Mem. College Sci. Kyoto Imperial Univ., **4**, p. 159; 1920.

[29] K. Akad. Wet. Amsterdam, **37**, p. 553; 1928. Zeit. für Physik, **48**, p. 62; 1928. Zeit. für Physik, **51**, p. 101; 1928.

[30] Science, **69**, p. 47; 1929. K. Akad. Wet. Amsterdam, **37**, p. 984; 1928. Zeit. für Physik, **53**, p. 658; 1929.

TABLE 11.—*Comparison of Cl I with A II and K III*

Term	Cl I	A II	K III
$3p\ {}^2P_{2,1}$	881	1, 431	2, 164
$4s\ {}^4P_{3,2}$	530. 20	844. 40	1, 265. 9
$4s\ {}^4P_{2,1}$	338. 44	515. 70	773. 5
$4s\ {}^2P_{2,1}$	639. 80	1, 014. 74	1, 506. 9
$4p\ {}^4P_{3,2}$	212. 05	307. 75	400. 2
$4p\ {}^4P_{2,1}$	233. 96	357. 30	542. 9
$4p\ {}^4D_{4,3}$	238. 26	439. 36	613. 6
$4p\ {}^4D_{3,2}$	353. 01	494. 57	721. 8
$4p\ {}^4D_{2,1}$	203. 36	260. 32	361. 4
$4p\ {}^2D_{3,2}$	340. 35	663. 90	995. 3
$4p\ {}^2P_{2,1}$	475. 40	−532. 96	
$3d\ {}^4D_{4,3}$	85. 92	153. 98	
$3d\ {}^4D_{3,2}$	110. 75	149. 62	
$3d\ {}^4D_{2,1}$	98. 02	107. 03	

The term $5p\ {}^2P_{2,1}$ of Cl I has not been found in A II. In both spectra it is to be seen that the term separations $4p\ {}^4P_{3,2}$ are smaller than $4p\ {}^4P_{2,1}$. It was these facts which led to the coordination of the term sequences with series limits discussed above. These anomalies are already apparent in the corresponding spectra of F I and Ne II, where the separations in the analogous terms $3p\ {}^4P_{3,2,1}$ show marked deviations from Landé's interval rule, although ${}^4P_{2,1}$ is actually smaller than ${}^4P_{3,2}$.

In both Cl I and A II the terms $4s\ {}^4P_{3,2,1}$ exhibit normal coupling; that is, the separations ${}^4P_{3,2}$ are larger than ${}^4P_{2,1}$ and approximately in the ratio required by the interval rule. In A II, however, the term $5s\ {}^4P_{3,2,1}$ shows abnormal coupling, $\Delta\nu_{3,2} = 627.76$, and $\Delta\nu_{2,1} = 729.14$. Although the corresponding term of Cl I has not been located, the $5s \rightarrow 4p$ combinations coming far in the infra-red, yet we may with confidence expect it to show the same anomaly as in A II, since in the following member of the sequence, $6s\ {}^4P_{3,2,1}$, the effect is quite pronounced. Here $\Delta\nu_{3,2} = 242.83$ and $\Delta\nu_{2,1} = 619.76$, the total separation being nearly the same as that of $4s\ {}^4P$.

Comparison of the term diagrams of Cl I and A II illustrates further the increasing stability, with increasing nuclear charge, of electron configurations containing *d* electrons. For Cl I the terms above the ground state in the order of stability are those from the 4*s*, 4*p* (5*s*), 5*p*, 3*d*, etc., electrons. The multiplets coming from the 3*d* terms are relatively weak and incomplete. For A II, however, the 3*d* terms appear immediately after the 4*s* terms and give rise to prominent multiplets. Cl I and A II thus illustrate the atomic property which led Bohr [31] to predict a ${}^2D$ term as lowest in Sc III from the increasing stability of the 3_3 orbits revealed by a comparison of Ca II with K I. More recently Laporte [32] has pointed out a similar property of the heavier atoms of the second long period, and Laporte and Lang[33] have shown that it exists for the isoelectronic systems of Ni, Cu^+, and Zn^{++}.

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[31] Zeit. für Physik. 9, p. 46; 1922.

[32] J. Opt. Soc. Am., 13, p. 1; 1926.

V. CONCLUSION AND ACKNOWLEDGMENTS

A count of the lines of Table 1 shows that 62 per cent of them have been classified on the basis of the terms of Table 3. Of those remaining unclassified, only a few may be designated as strong lines. Three of these lie in the infra-red and two in the orange. All the other unclassified lines are faint and show on the spectrograms only after long exposures. The group of faint lines between 8260 and 8300 A is only incompletely measured. The original spectrogram shows a group of very close lines (fine-structure groups?) of which it was possible to see only the stronger ones under the measuring microscope. Not all of the faint lines in the table may be emitted by the Cl atom, but, in view of the fact that many of them represent permissible term combinations, all that have been measured are retained in the present list to await the test of future observations. These faint lines, if real, may owe their origin to the terms coming from ^1S and ^1D of the ion, but not yet established.

The question as to the existence of chlorine in the sun's reversing layer may now be answered. It was natural for astrophysicists to look toward the lighter halogens as a possible origin for the numerous unidentified Fraunhofer lines. But, as we have seen from the foregoing analysis of the Cl spectrum, the only lines that might be likely to occur are those from the $4p \rightarrow 4s$ transition, and these all lie in the near infra-red. Comparing the wave lengths of Table 1 with those of the sun presented in the recent Mount Wilson Revision of Rowland's Preliminary Table of Solar Spectrum Wave Lengths,[34] it is seen that only a few of the relatively faint chlorine lines are in approximate agreement with solar lines. These lines are not of the class of ultimate or penultimate lines, as defined by Russell,[35] and we must, therefore, conclude that there is no evidence at present for the existence of chlorine in the sun.

In addition to extending our knowledge of the arc spectrum of chlorine the experiments on which this paper is based have also yielded wave-length data for the spark spectra emitted by the singly and doubly ionized ions. We have made some progress in the classification of these lines and expect to give a report of this work, in the near future, in this journal.

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[33] Phys. Rev., **30**, p. 378; 1927.

[34] Carnegie Institution of Washington Publication No. 396; 1928.

[35] Astrophys. Jl., **61**, p. 223; 1925.

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WASHINGTON, February 20, 1929.

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